Summary of the Work

Polyaniline has unique properties such as high conductivity upon protonation, good environmental stability, and easy and low cost of synthesis. However, it suffers from intractability and insolubility which is also true of other conducting polymers. Among the various efforts made to improve the solubility, copolymerization of aniline with soluble derivatives of aniline has not been studied in detail. For applications ranging from antistatic agents, shielding materials to biosensors, the solubility of polyaniline plays a more important role than its conductivity.

The studies on the synthesis and characterization by different physical techniques, of the copolymers of aniline and toluidine, and of aniline/toluidine with aniline derivatives such as aminoacetophenone, chloroaniline, nitroaniline etc are presented and discussed. Three pathways have been tried for synthesis of copolymers. They are the solution, emulsion and inverse emulsion methods. In the conventional solution method, aqueous solutions of the dopant, the oxidant and the monomers are reacted together. This method has been most widely used for the synthesis of the homopolymers as well as copolymers of aniline. In recent years, emulsion and inverse emulsion polymerization of aniline has come to the forefront. In inverse emulsion polymerization an aqueous solution of the monomer is emulsified in a non-polar organic solvent, chloroform for example in the present study, and the polymerisation is initiated with an oil - soluble initiator. Inverted emulsion method using benzoyl peroxide as a novel mild oxidant was also employed to synthesize the copolymers.

Poly(aniline-*co*-*o*-toluidine) and poly(aniline-*co*-*m*-toluidine) copolymers of different compositions have been synthesized and characterized. The synthesis has been carried out by both solution, and inverse emulsion methods, using ammonium persulphate and benzoyl peroxide as the oxidants respectively, by chemical oxidative copolymerization of aniline with *o*-toluidine and *m*-toluidine, in order to understand the

effect of synthesis conditions on the properties of the copolymers obtained. The compositions of the copolymers have been determined by infrared and ^{1}H NMR spectroscopy. The results showed that the actual content of the toluidine units in the copolymer is higher than the feed content of toluidine. The conductivity of the copolymers varies in the broad range of 1.6 to 3.2 x 10^{-3} Scm^{-1}. The copolymers exhibit lower thermal decomposition temperatures than the homopolymers, poly(*o*-toluidine) and poly(*m*-toluidine). The properties of the copolymers are influenced by the amount of toluidine in the copolymer. The copolymers show better solubility than polyaniline. Copolymers of *o*-toluidine and *m*-toluidine with aniline show different solvatochromic properties.

The synthesis of copolymers of aniline with *o/m*– aminoacetophenone was carried out by solution, emulsion and inverse emulsion methods. Although *o/m*–aminoacetophenone does not homopolymerize, their copolymers could easily be prepared. Solution copolymerization of aniline with *o-/m*-aminoacetophenone gave copolymers of low conductivity and thermal stability. The emulsion and inverted emulsion procedures were hence utilized for the synthesis of soluble conductive copolymers of aniline with *o-/m*-aminoacetophenone of different compositions. The influence of the synthesis conditions, such as the solvent, non-solvent, the oxidant and the temperature used for carrying out the polymerization, on the properties of the copolymers obtained has been studied by spectral, thermal, electrical and morphological techniques. The copolymer compositions determined by the ^{1}H NMR spectroscopy indicate a lower reactivity ratio for *m*-aminoacetophenone than for aniline in the case of emulsion polymerization while the reverse seems to hold true for the inverse emulsion polymerization. The copolymers formed by the emulsion polymerization are random type as determined by the Finemann-Ross method. The characteristic features of these copolymers are good solubility and higher conductivity relative to the copolymers of aniline with other carboxylate derivatives. The results have been interpreted on the basis of the effect of the -$COCH_3$ substituent on the copolymer structure.

The above work has been extended to the study of copolymers of *o*-toluidine/*m*-toluidine with *o*-/*m*-aminoacetophenone. A series of poly(*o*-/*m*-toluidine-*co*-*o*-/*m*-aminoacetophenone) copolymers have been synthesized and characterized. The copolymers were synthesized by the emulsion and inverse emulsion methods. Although aminoacetophenone does not homopolymerize, the copolymers of aminoacetophenone and toluidine could also be readily prepared under conditions used for the polymerization of aniline. The influence of the polymerization conditions such as the monomer feed ratios, solvent and the non-solvent has been investigated. The composition of the resulting copolymers has been determined by ^{1}H NMR spectroscopy. The conductivity of the copolymers varies with the aminoacetophenone content in the feed and on the polymerization conditions. The copolymers of toluidines with *o*-/*m*-aminoacetophenone have conductivities an order of magnitude higher than that of the homopolymer polytoluidine. These copolymers were found to have increased particle size from their scanning electron micrographs and good solubility compared to the homopolymer polytoluidines. The copolymers synthesized using toluene as solvent medium by both the methods are more conducting than those synthesized in chloroform.

Fully substituted polyaniline derivatives were synthesized by chemical copolymerization of *o*-toluidine with *o*-chloroaniline by three different methods to note the effect of synthesis conditions. Subsequently, a series of poly(*o*-/*m*-toluidine-*co*-*o*-/*m*-chloroaniline) copolymers of different compositions were synthesized by the emulsion method which was found to give copolymers with good solubility and conductivity, using ammonium persulphate as the oxidant. The effect of the concentration of each of the monomers on the copolymers formed is analyzed by varying the monomer feed compositions. Although homopolymerization of *o*-chloroaniline requires a stronger oxidising agent, chromic acid in HCl, the copolymers of *o*-chloroaniline and toluidine could be readily synthesized using milder oxidants, such as benzoyl peroxide and ammonium persulphate under conditions used for the polymerization of aniline. The conductivity of the copolymers was found to be 2 to5 orders magnitude higher compared

to that of the homopolymers poly(*o*-toluidine) and poly(*m*-chloroaniline), and a copolymer of *o*-toluidine and *m*-chloroaniline exhibited conductivity as high as of 0.14 S cm^{-1}. The conductivity of these copolymers is even higher than that of the aniline copolymer, poly(aniline-*co*-chloroaniline). All the copolymers are completely soluble in polar solvents such as DMSO and show higher heat stability with increasing chloroaniline content. These effects could be interpreted in terms of extensive hydrogen bonding and interchain linking and also as due to increased electron delocalization in these copolymers due to the presence electron rich toluidine ring adjacent to electron deficient chloroaniline.

The effect of increasing the electron withdrawing nature of the acceptor group in the aniline derivative was investigated by synthesizing copolymers of *o*-/*m*-toluidine with *o*-nitroaniline. Although *o*-nitroaniline does not homopolymerize, its copolymers with *o*-/*m*-toluidine could readily be synthesized. The copolymers show good conductivity and better solubility than the homopolymers (polytoluidines) and have comparatively higher thermal stability. The effect of the substituents on the properties of the copolymers is studied. For toluidine and chloroaniline copolymers, since the size of the substituent methyl group is almost the same as that of the chloro group, the properties of the copolymers are apparently influenced chiefly by the electronic effects.

Two series of terpolymers have been prepared – those of *o*-/*m*-toluidine and aniline with *o*-aminobenzoic acid, and *o*-/*m*-toluidine, aniline with *m*-aminobenzenesulphonic acid, using emulsion polymerization. The exhibit high conductivity (~1 Scm^{-1}) and possess higher thermal stability compared to that of polyaniline. This could be explained as due to the presence of internal doping groups which also increases hydrogen bonding and interchain linking. The terpolymers help to investigate the reactivities of the electron donor and electron acceptor monomers in the presence of aniline.